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PART III

ENVIRONMENTAL PROTECTION AGENCY

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STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

Petroleum Refinery Claus Sulfur Recovery Plants

[6560-01]

Title 40—Protection of Environment

CHAPTER I—ENVIRONMENTAL PROTECTION AGENCY

SUBCHAPTER C—AIR PROGRAMS

[FRL 836-1]

PART 60—STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

Petroleum Refinery Claus Sulfur Recovery Plants

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This rule establishes standards of performance which will limit emissions of sulfur dioxide (SO_2) and reduced sulfur compounds from new, modified, and reconstructed petroleum refinery Claus sulfur recovery plants. The standards implement the Clean Air Act and are based on the Administrator's determination that emissions from petroleum refinery Claus sulfur recovery plants contribute significantly to air pollution. The intended effect of the standards is to require new, modified, and reconstructed petroleum refinery Claus sulfur recovery plants to use the best technological system of continuous emission reduction.

EFFECTIVE DATE: March 15, 1978.

ADDRESSES: Copies of the standard support documents are available on request from the U.S. EPA Library (MD-35), Research Triangle Park, N.C. 27711. The requestor should specify "Standards Support and Environmental Impact Statement, Volume I: Proposed Standards of Performance for Petroleum Refinery Sulfur Recovery Plants" (EPA-450/2-76-016a) and/or "Standards Support and Environmental Impact Statement, Volume II: Promulgated Standards of Performance for Petroleum Refinery Sulfur Recovery Plants" (EPA-450/2-76-016b). Comment letters responding to the proposed rules published in the FEDERAL REGISTER on October 4, 1976 (41 FR 43866), are available for public inspection and copying at the U.S. Environmental Protection Agency, Public Information Reference Unit (EPA Library), Room 2922, 401 M Street SW., Washington, D.C.

FOR FURTHER INFORMATION CONTACT:

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SUPPLEMENTARY INFORMATION:

SUMMARY

On October 4, 1976 (41 FR 43866), EPA proposed standards of performance for new petroleum refinery Claus sulfur recovery plants under section 111 of the Clean Air Act, as amended. The promulgated standards are essentially the same as those proposed, although an exemption for small petroleum refineries has been included in the promulgated standards. The standards are based on the use of tail gas scrubbing systems which have been determined to be the best technological system of continuous emission reduction, taking into consideration the cost of achieving such emission reduction, any nonair quality, health, and environmental impact and energy requirements. Compliance with these standards will increase the overall sulfur recovery efficiency of a typical refinery Claus sulfur recovery plant to about 99.9 percent, compared to a recovery efficiency of about 94 percent for an uncontrolled refinery Claus sulfur recovery plant, or a recovery efficiency of about 99 percent for a Claus sulfur recovery plant complying with typical State emission control regulations for these plants.

The promulgated standards will apply to: (1) any Claus sulfur recovery plant with a sulfur production capacity of more than 20 long tons per day (LTD) which is associated with a small petroleum refinery (i.e., a petroleum refinery having a crude oil processing capacity of 50,000 barrels per stream day (BSD) or less which is owned or controled by a refiner whose total combined crude oil processing capacity is 137,500 BSD or less) and (2) any size Claus sulfur recovery plant associated with a large petroleum refinery. Specifically, the standards limit the concentration of sulfur dioxide (SO_2) in the gases discharged into the atmosphere to 0.025 percent by volume at zero percent oxygen on a dry basis. Where the emission control system installed to comply with these standards discharges residual emissions of hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2), the standards limit the concentration of H_2S and the total concentration of H_2S, COS and CS_2 (calculated as SO_2) in the gases discharged into the atmosphere to 0.0010 percent and 0.030 percent by volume at zero percent oxygen on a dry basis, respectively.

Compliance with these standards will reduce nationwide sulfur dioxide emissions by some 55,000 tons per year by 1980. This reduction will be achieved without any significant adverse impact on other aspects of environmental quality, such as solid waste disposal, water pollution, or noise. This reduction in emissions will also be accompanied by a reduction in the growth of nationl energy consumption equivalent to about 90,000 barrels of fuel oil per year by 1980.

The economic impact of the promulgated standards is reasonable. They will result in an increase in the annual operating costs of the petroleum refining industry by some $16 million per year in 1980. An individual refiner who installs alternative II controls will need to increase his prices from 0.1 to 1 percent to maintain his profitability.

It should be noted that standards of performance for new sources established under section 111 of the Act reflect the degree of emission limitation achievable through application of the best adequately demonstrated technological system of continuous emission reduction (taking into consideration the cost of achieving such emission reduction, any nonair quality health and environmental impact and energy requirements). State implementation plans (SIPs) approved or promulgated under section 110 of the Act, on the other hand, must provide for the attainment and maintenance of national ambient air quality standards (NAAQS) designed to protect public health and welfare. For that purpose, SIPs must in some cases require greater emission reduction than those required by standards of performance for new sources. Section 173(2) of the Act requires, among other things, that a new or modified source constructed in an area which exceeds the NAAQS must reduce emissions to the level which reflects the "lowest achievable emission rate" for such category of source, unless the owner or operator demonstrates that the source cannot achieve such an emission rate. In no event can the emission rate exceed any applicable standard of performance.

A similar situation may arise when a major emitting facility is to be constructed in a geographic area which falls under the prevention of significant deterioration of air quality provisions of the Act (part C). These provisions require, among other things, that major emitting facilities to be constructed in such areas are to be subject to the best available control technology. The term "best available control technology" (BACT) means "an emission limitation based on the maximum degree of reduction of each pollutant subject to regulation under this Act emitted from or which results from any major emitting facility, which the permitting authority, on a case-by-case basis, taking into account energy, environmental, and economic impacts and other costs, determines is achievable for such facility through application of production processes and available methods, systems, and techniques, including fuel cleaning or treatment or innovative fuel combustion techniques for control of each such pollutant. In no event shall appli-

cation of 'best available control technology' result in emissions of any pollutants which will exceed the emissions allowed by any applicable standard established pursuant to section 111 or 112 of this Act."

Standards of performance should not be viewed as the ultimate in achievable emission control and should not preclude the imposition of a more stringent emission standard, where appropriate. For example, while cost of achievement may be an important factor in determining standards of performance applicable to all areas of the country (clean as well as dirty), costs must be accorded far less weight in determining the "lowest achievable emission rate" for new or modified sources locating in areas violating statutorily-mandated health and welfare standards. Although there may be emission control technology available that can reduce emissions below those levels required to comply with standards of performance, this technology might not be selected as the basis of standards of performance due to costs associated with its use. This in no way should preclude its use in situations where cost is a lesser consideration, such as determination of the "lowest achievable emission rate."

In addition, States are free under section 116 of the Act to establish even more stringent emission limits than those established under section 111 or those necessary to attain or maintain the NAAQS under section 110. Thus, new sources may in some cases be subject to limitations more stringent than standards of performance under section 111, and prospective owners and operators of new sources should be aware of this possibility in planning for such facilities.

Public Participation

Prior to proposal of the standards, interested parties were advised by public notice in the Federal Register of a meeting of the National Air Pollution Control Techniques Advisory Committee to discuss the standards recommended for proposal. This meeting was open to the public and each person attending was given ample opportunity to comment on the standards recommended for proposal. The standards were proposed on October 4, 1976, and copies of the proposed standards and the Standards Support and Environmental Impact Statement (SSEIS) were distributed to members of the petroleum refining industry and several environmental groups at this time. The public comment period extended from October 4, 1976, to December 3, 1976.

Twenty-two comment letters were received on the proposed standards of performance. These comments have been carefully considered and, where determined to be appropriate by the Administrator, changes have been made in the standards which were proposed.

Major Comments

Comments on the proposed standards were received from several oil industry representatives, State and local air pollution control agencies, a vendor of emission source testing equipment, and several Federal agencies. These comments covered four major areas: the costs of implementing the standards, the ability of emission control technology to meet the standards, the environmental impacts of the standards, and the energy impacts of the standards.

COSTS

The major comments concerning costs were that the costs of the emission control systems required to meet the standards were underestimated, that these costs were excessive; and that small sulfur recovery plants, or small petroleum refineries should be exempt from the standard.

The basic cost data used to develop the cost estimates were obtained from pretroleum refinery sources. No specific data or information was provided in the public comments, however, which would indicate that these costs are significantly in error.

In the preamble to the proposed standards, comments were specifically invited concerning the impact of the standards on the small refiner. After considering these comments, EPA has concluded that some relief from the standards is appropriate. The major factor involved in this decision was a consideration of the cost effectiveness of the standards on large and small refiners. The incremental cost per incremental unit of sulfur emissions that must be controlled to meet the standards is substantially greater for the small refiner than for the large refiner. Furthermore, the impact of these costs on the small refiner is more severe than the impact on the large refiner, because the small refiner cannot readily pass on the cost of emission control equipment. Consequently, as discussed in volume II of the Standards Support and Environmental Impact Statement (SSEIS), the promulgated standards include a lower size cutoff for small petroleum refineries and Claus sulfur recovery plants. Claus sulfur recovery plants with a sulfur production capacity of 20 long tons per day or less associated with a petroleum refinery with a crude oil processing capacity of 50,000 BSD or less, which is owned or controlled by a refiner whose total combined crude oil processing capacity is 137,500 BSD or less, are exempt from the standards. This definition of a small petroleum refinery is consistent with that included in section 211 of the Clean Air Act, as amended.

EMISSION CONTROL TECHNOLOGY

A major concern of many commenters was the limited amount of source test data used in support of the numerical emission limits included in the standards and the fact that some of these data were collected at refineries where the emission control system was operating below design capacity. Also, some commenters questioned the ability of the alternative II emission control systems to continuously operate at a 99.9 percent control efficiency because of the adverse impact of Claus sulfur recovery plant fluctuations and CO_2-rich waste gas streams.

In arriving at the numerical emissions limits included in the standards, source test data collected by a local agency at times when the emission control systems were operating at normal capacities, information from vendors of emission control equipment, published literature on emission control technology, and contractor reports on the performance of emission control technology were considered, in addition to the data collected during EPA's source tests. Based on the information and data from these sources and the lack of any new information and data submitted by the commenters, no change in the emission limits of the standards is warranted. Furthermore, the numerical emission limits in the standards contain an adequate safety margin to allow for increased emissions due to Clause sulfur recovery plant fluctuations.

With repect to the potential adverse impact of high CO_2 gas streams, this is not likely to impair the overall emission control system efficiency since high CO_2 gas streams are seldom found in the gases treated in refinery Claus sulfur recovery plants.

ENVIRONMENTAL IMPACT

Several commenters felt that the assessment of the environmental impact of the standards was, in some cases, biased and not always clear. One of these commenters suggested that a thorough environmental impact statement should be prepared to clarify the impacts of the standards.

Litigation involving standards of performance has established that preparation of a formal environmental impact statement under the National Environmental Policy Act is not necessary for actions under section 111 of the Clean Air Act. While a formal environmental impact statement is not prepared, the beneficial as well as the adverse impacts of standards of performance are considered. The promulgated standards will significantly reduce emissions of sulfur from petroleum refineries without resulting in any significant adverse environmental, energy, or economic impacts.

Other commenters felt that standards based on 99 percent control (al-

ternative I) would be essentially as environmentally beneficial as standards based on 99.9 percent control and would be less costly to the public. This argument was based on the premise that most State regulations do not require control of Claus sulfur plant emissions at the 99 percent level as claimed in volume I of the SSEIS. Hence, standards based on alternative I would significantly reduce national sulfur emissions from refinery Claus sulfur recovery plants.

A review of State regulations for controlling emissions from refinery sulfur recovery plants has shown that the majority of the States with the largest petroleum refining capacities require 99 percent control of emissions from new and existing sulfur recovery plants. Since refinery sulfur recovery plant growth will likely occur in these States, the conclusion that standards based on 99 percent control would have little or no beneficial impact is essentially correct.

ENERGY IMPACT

Several commenters questioned the conclusion that compliance with standards based on alternative II could lead to an energy savings, compared to standards based on alternative I. A review of the information and data available confirms this conclusion. In any case, the important consideration is whether the energy impact of the standards is reasonable. No information was submitted which would indicate that the energy impact of the standards is unreasonable.

OTHER CONSIDERATIONS

At proposal comments were requested relative to EPA's decision to regulate reduced sulfur compound emissions, which are designated pollutants, without implementing section 111(d) of the Clean Air Act at this time. The one commenter who responded to this issue was in agreement with this decision.

As discussed in both the preamble to the proposed standards and volumes I and II of the SSEIS, petroleum refinery Claus sulfur recovery plants are sources of SO_2 emissions, not reduced sulfur compound emissions. One of the emission control technologies for reducing SO_2 emissions, however, first converts these emissions to reduced sulfur compounds and then controls these compounds. Consequently, this technology may discharge residual emissions of reduced sulfur compounds to the atmosphere.

Currently, there are about 30 refinery Claus sulfur recovery plants in the United States which have installed reduction emission control systems to reduce SO_2 emissions. A review of these plants indicates that these emission control systems are well designed and well maintained and operated. Emissions of reduced sulfur compounds are less than 0.050 percent (i.e., 500 ppm), which is only slightly higher than the numerical emission limit included in the promulgated standard. Thus, there is little to gain at this time by requiring States to develop regulations limiting emissions from these sources. Consequently, section 111(d) will not be implemented until resources permit, taking into consideration other requirements of the Clean Air Act, as amended, which EPA must implement.

Several commenters were concerned that Reference Method 15 might not be practical for use in a refinery environment. The basis for most of these objections was that the commenters thought this method was being proposed as a continuous monitoring method. However, Reference Method 15 was not proposed for use as a continuous monitoring method. Performance specifications for continuous monitors for reduced sulfur compounds have not been developed and therefore such monitors are not required to be installed until performance specifications for these monitors are proposed and promulgated under Appendix B of 40 CFR Part 60.

Reference Method 15 has been revised to allow greater flexibility in operating details and equipment choice. The user is now permitted to design his own sampling and analysis system as long as he preserves the operating principle of gas chromatography with flame photometric detection and meets the design and performance criteria.

MISCELLANEOUS

The effective date of this regulation is March 15, 1978. Section 111(b)(1)(B) of the Clean Air Act provides that standards of performance or revisions of them become effective upon promulgation and apply to affected facilities, construction or modification of which was commenced after the date of proposal (October 4, 1976).

ECONOMIC IMPACT ASSESSMENT: An economic assessment has been prepared as required under section 317 of the Act. This also satisfies the requirements of Executive Orders 11821 and 11949 and OMB Circular A-107.

Dated: March 1, 1978.

DOUGLAS M. COSTLE,
Administrator.

1. Section 60.100 is amended as follows:

§ 60.100 Applicability and designation of affected facility.

(a) The provisions of this subpart are applicable to the following affected facilities in petroleum refineries: fluid catalytic cracking unit catalyst regenerators, fuel gas combustion devices, and all Claus sulfur recovery plants except Claus plants of 20 long tons per day (LTD) or less associated with a small petroleum refinery. The Claus sulfur recovery plant need not be physically located within the boundaries of a petroleum refinery to be an affected facility, provided it processes gases produced within a petroleum refinery.

(b) Any fluid catalytic cracking unit catalyst regenerator of fuel gas combustion device under paragraph (a) of this section which commences construction or modification after June 11, 1973, or any Claus sulfur recovery plant under paragraph (a) of this section which commences construction or modification after October 4, 1976, is subject to the requirements of this part.

(Secs. 111 and 301(a), Clean Air Act, as amended (42 U.S.C. 7411, 7601 (a)), and additional authority as noted below.)

2. Section 60.101 is amended as follows:

§ 60.101 Definitions.

* * * * *

(i) "Claus sulfur recovery plant" means a process unit which recovers sulfur from hydrogen sulfide by a vapor-phase catalytic reaction of sulfur dioxide and hydrogen sulfide.

(j) "Oxidation control system" means an emission control system which reduces emissions from sulfur recovery plants by converting these emissions to sulfur dioxide.

(k) "Reduction control system" means an emission control system which reduces emissions from sulfur recovery plants by converting these emissions to hydrogen sulfide.

(l) "Reduced sulfur compounds" mean hydrogen sulfide (H_2S), carbonyl sulfide (COS) and carbon disulfide (CS_2).

(m) "Small petroleum refinery" means a petroleum refinery which has a crude oil processing capacity of 50,000 barrels per stream day or less, and which is owned or controlled by a refinery with a total combined crude oil processing capacity of 137,500 barrels per stream day or less.

3. Section 60.102 is amended by revising paragraph (a) introductory text and paragraph (b) as follows:

§ 60.102 Standard for particulate matter.

(a) On and after the date on which the performance test required to be conducted by § 60.8 is completed, no owner or operator subject to the provisions of this subpart shall discharge or cause the discharge into the atmosphere from any fluid catalytic cracking unit catalyst regenerator:

(1) * * *

(2) * * *

(b) Where the gases discharged by the fluid catalytic cracking unit catalyst regenerator pass through an in-

cinerator or waste heat boiler in which auxiliary or supplemental liquid or solid fossil fuel is burned, particulate matter in excess of that permitted by paragraph (a)(1) of this section may be emitted to the atmosphere, except that the incremental rate of particulate matter emissions shall not exceed 43.0 g/MJ (0.10 lb/million Btu) of heat input attributable to such liquid or solid fossil fuel.

4. Section 60.104 is amended as follows:

§ 60.104 Standard for sulfur dioxide.

(a) On and after the date on which the performance test required to be conducted by § 60.8 is completed, no owner or operator subject to the provisions of this subpart shall:

(1) Burn in any fuel gas combustion device any fuel gas which contains hydrogen sulfide in excess of 230 mg/dscm (0.10 gr/dscf), except that the gases resulting from the combustion of fuel gas may be treated to control sulfur dioxide emissions provided the owner or operator demonstrates to the satisfaction of the Administrator that this is as effective in preventing sulfur dioxide emissions to the atmosphere as restricting the H_2 concentration in the fuel gas to 230 mg/dscm or less. The combustion in a flare of process upset gas, or fuel gas which is released to the flare as a result of relief valve leakage, is exempt from this paragraph.

(2) Discharge or cause the discharge of any gases into the atmosphere from any Claus sulfur recovery plant containing in excess of:

(i) 0.025 percent by volume of sulfur dioxide at zero percent oxygen on a dry basis if emissions are controlled by an oxidation control system, or a reduction control system followed by incineration, or

(ii) 0.030 percent by volume of reduced sulfur compounds and 0.0010 percent by volume of hydrogen sulfide calculated as sulfur dioxide at zero percent oxygen on a dry basis if emissions are controlled by a reduction control system not followed by incineration.

(b) [Reserved]

5. Section 60.105 is amended as follows:

§ 60.105 Emission monitoring.

(a) * * *

(2) An instrument for continuously monitoring and recording the concentration of carbon monoxide in gases discharged into the atmosphere from fluid catalytic cracking unit catalyst regenerators. The span of this continuous monitoring system shall be 1,000 ppm.

(3) * * *

(4) An instrument for continuously monitoring and recording concentrations of hydrogen sulfide in fuel gases burned in any fuel gas combustion device, if compliance with § 60.104(a)(1) is achieved by removing H_2S from the fuel gas before it is burned; fuel gas combustion devices having a common source of fuel gas may be monitored at one location, if monitoring at this location accurately represents the concentration of H_2S in the fuel gas burned. The span of this continuous monitoring system shall be 300 ppm.

(5) An instrument for continuously monitoring and recording concentrations of SO_2 in the gases discharged into the atmosphere from any Claus sulfur recovery plant if compliance with § 60.104(a)(2) is achieved through the use of an oxidation control system or a reduction control system followed by incineration. The span of this continuous monitoring system shall be sent at 500 ppm.

(6) An instrument(s) for continuously monitoring and recording the concentration of H_2S and reduced sulfur compounds in the gases discharged into the atmosphere from any Claus sulfur recovery plant if compliance with § 60.104(a)(2) is achieved through the use of a reduction control system not followed by incineration. The span(s) of this continuous monitoring system(s) shall be set at 20 ppm for monitoring and recording the concentration of H_2S and 600 ppm for monitoring and recording the concentration of reduced sulfur compounds.

* * * * *

(e) * * *

(1) * * *

(2) Carbon monoxide. All hourly periods during which the average carbon monoxide concentration in the gases discharged into the atmosphere from any fluid catalytic cracking unit catalyst regenerator subject to § 60.103 exceeds 0.050 percent by volume.

(3) Sulfur dioxide. (i) Any three-hour period during which the average concentration of H_2S in any fuel gas combusted in any fuel gas combustion device subject to § 60.104(a)(1) exceeds 230 mg/dscm (0.10 gr/dscf), if compliance is achieved by removing H_2S from the fuel gas before it is burned; or any three-hour period during which the average concentration of SO_2 in the gases discharged into the atmosphere from any fuel gas combustion device subject to § 60.104(a)(1) exceeds the level specified in § 60.104(a)(1), if compliance is achieved by removing SO_2 from the combusted fuel gases.

(ii) Any twelve-hour period during which the average concentration of SO_2 in the gases discharged into the atmosphere from any Claus sulfur recovery plant subject to § 60.104(a)(2) exceeds 250 ppm at zero percent oxygen on a dry basis if compliance with § 60.104(b) is achieved through the use of an oxidation control system or a reduction control system followed by incineration; or any twelve-hour period during which the average concentration of H_2S, or reduced sulfur compounds in the gases discharged into the atmosphere of any Claus sulfur plant subject to § 60.104(a)(2)(b) exceeds 10 ppm or 300 ppm, respectively, at zero percent oxygen and on a dry basis if compliance is achieved through the use of a reduction control system not followed by incineration.

6. Section 60.106 is amended as follows:

§ 60.106 Test methods and procedures.

* * * * *

(c) For the purpose of determining compliance with § 60.104(a)(1), Method 11 shall be used to determine the concentration of H_2S and Method 6 shall be used to determine the concentration of SO_2.

(1) If Method 11 is used, the gases sampled shall be introduced into the sampling train at approximately atmospheric pressure. Where refinery fuel gas lines are operating at pressures substantially above atmosphere, this may be accomplished with a flow control valve. If the line pressure is high enough to operate the sampling train without a vacuum pump, the pump may be eliminated from the sampling train. The sample shall be drawn from a point near the centroid of the fuel gas line. The minimum sampling time shall be 10 minutes and the minimum sampling volume 0.01 dscm (0.35 dscf) for each sample. The arithmetic average of two samples of equal sampling time shall constitute one run. Samples shall be taken at approximately 1-hour intervals. For most fuel gases, sample times exceeding 20 minutes may result in depletion of the collecting solution, although fuel gases containing low concentrations of hydrogen sulfide may necessitate sampling for longer periods of time.

(2) If Method 6 is used, Method 1 shall be used for velocity traverses and Method 2 for determining velocity and volumetric flow rate. The sampling site for determining SO_2 concentration by Method 6 shall be the same as for determining volumetric flow rate by Method 2. The sampling point in the duct for determining SO_2 concentration by Method 6 shall be at the centroid of the cross section if the cross sectional area is less than 5 m^2 (54 ft^2) or at a point no closer to the walls than 1 m (39 inches) if the cross sectional area is 5 m^2 or more and the centroid is more than one meter from the wall. The sample shall be extracted at a rate proportional to the gas velocity at the sampling point. The minimum sampling time shall be 10 minutes and the minimum sampling volume 0.01 dscm (0.35 dscf) for each sample. The arithmetic average of two

samples of equal sampling time shall constitute one run. Samples shall be taken at approximately 1-hour intervals.

(d) For the purpose of determining compliance with § 60.104(a)(2), Method 6 shall be used to determine the concentration of SO_2 and Method 15 shall be used to determine the concentration of H_2S and reduced sulfur compounds.

(1) If Method 6 is used, the procedure outlined in paragraph (c)(2) of this section shall be followed except that each run shall span a minimum of four consecutive hours of continuous sampling. A number of separate samples may be taken for each run, provided the total sampling time of these samples adds up to a minimum of four consecutive hours. Where more than one sample is used, the average SO_2 concentration for the run shall be calculated as the time weighted average of the SO_2 concentration for each sample according to the formula:

$$C_R = \sum_{i=1}^{N} C_{S_i} \frac{t_{S_i}}{T}$$

Where:

C_R = SO_2 concentration for the run.
N = Number of samples.
C_{Si} = SO_2 concentration for sample i.
t_{Si} = Continuous sampling time of sample i.
T = Total continuous sampling time of all N samples.

(2) If Method 15 is used, each run shall consist of 16 samples taken over a minimum of three hours. The sampling point shall be at the centroid of the cross section of the duct if the cross sectional area is less than 5 m^2 (54 ft^2) or at a point no closer to the walls than 1 m (39 inches) if the cross sectional area is 5 m^2 or more and the centroid is more than 1 meter from the wall. To insure minimum residence time for the sample inside the sample lines, the sampling rate shall be at least 3 liters/minute (0.1 ft^3/min). The SO_2 equivalent for each run shall be calculated as the arithmetic average of the SO_2 equivalent of each sample during the run. Reference Method 4 shall be used to determine the moisture content of the gases. The sampling point for Method 4 shall be adjacent to the sampling point for Method 15. The sample shall be extracted at a rate proportional to the gas velocity at the sampling point. Each run shall span a minimum of four consecutive hours of continuous sampling. A number of separate samples may be taken for each run provided the total sampling time of these samples adds up to a minimum of four consecutive hours. Where more than one sample is used, the average moisture content for the run shall be calculated as the time weighted average of the moisture content of each sample according to the formula:

$$B_{wo} = \sum_{i=1}^{N} B_{si} \left[\frac{t_{si}}{T}\right]$$

B_{wo} = Proportion by volume of water vapor in the gas stream for the run.
N = Number of samples.
B_{si} = Proportion by volume of water vapor in the gas stream for the sample i.
t_{si} = Continuous sampling time for sample i.
T = Total continuous sampling time of all N samples.

(Sec. 114 of the Clean Air Act, as amended [42 U.S.C. 7414]).

* * * * *

Appendix A—Reference Methods

7. Appendix A is amended by adding a new reference method as follows:

Method 15. Determination of Hydrogen Sulfide, Carbonyl Sulfide, and Carbon Disulfide Emissions From Stationary Sources

INTRODUCTION

The method described below uses the principle of gas chromatographic separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent usable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that the criteria set below are met.

1. Principle and applicability

1.1 Principle. A gas sample is extracted from the emission source and diluted with clean dry air. An aliquot of the diluted sample is then analyzed for hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2) by gas chromatographic (GC) separation and flame photometric detection (FPD).

1.2 Applicability. This method is applicable for determination of the above sulfur compounds from tail gas control units of sulfur recovery plants.

2. Range and sensitivity

2.1 Range. Coupled with a gas chromtographic system utilizing a 1-milliliter sample size, the maximum limit of the FPD for each sulfur compound is approximately 10 ppm. It may be necessary to dilute gas samples from sulfur recovery plants hundredfold (99:1) resulting in an upper limit of about 1000 ppm for each compound.

2.2 The minimum detectable concentration of the FPD is also dependent on sample size and would be about 0.5 ppm for a 1 ml sample.

3. Interferences

3.1 Moisture Condensation. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This potential is eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

3.2 Carbon Monoxide and Carbon Dioxide. CO and CO_2 have substantial desensitizing effects on the flame photometric detector even after 9:1 dilution. (Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluding CO and CO_2 before any of the sulfur compounds to be measured.) Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in the diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatographs should show agreement within the precision limits of section 4.1.

3.3 Elemental Sulfur. The condensation of sulfur vapor in the sampling line can lead to eventual coating and even blockage of the sample line. This problem can be eliminated along with the moisture problem by heating the sample line.

4. Precision

4.1 Calibration Precision. A series of three consecutive injections of the same calibration gas, at any dilution, shall produce results which do not vary by more than ±13 percent from the mean of the three injections.

4.2 Calibration Drift. The calibration drift determined from the mean of three injections made at the beginning and end of any 8-hour period shall not exceed ±5 percent.

5. Apparatus

5.1.1 Probe. The probe must be made of inert material such as stainless steel or glass. It should be designed to incorporate a filter and to allow calibration gas to enter the probe at or near the sample entry point. Any portion of the probe not exposed to the stack gas must be heated to prevent moisture condensation.

5.1.2 The sample line must be made of Teflon,[1] no greater than 1.3 cm (½ in) inside diameter. All parts from the probe to the dilution system must be thermostatically heated to 120° C.

5.1.3 Sample Pump. The sample pump shall be a leakless Teflon coated diaphragm type or equivalent. If the pump is upstream of the dilution system, the pump head must be heated to 120° C.

5.2 Dilution System. The dilution system must be constructed such that all sample contacts are made of inert material (e.g. stainless steel or Teflon). It must be heated to 120° C and be capable of approximately a 9:1 dilution of the sample.

5.3 Gas Chromatograph. The gas chromatograph must have at least the following components:

5.3.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±1° C.

5.3.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature ±1° C.

5.3.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

5.3.4 Flame Photometric Detector.

5.3.4.1 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

5.3.4.2 Power Supply. Capable of delivering up to 750 volts.

5.3.4.3 Recorder. Compatible with the output voltage range of the electrometer.

[1] Mention of trade names or specific products does not constitute an endorsement by the Environmental Protection Agency.

5.4 Gas Chromatograph Columns. The column system must be demonstrated to be capable of resolving three major reduced sulfur compounds: H_2S, COS, and CS_2.

To demonstrate that adequate resolution has been achieved the tester must submit a chromatograph of a calibration gas containing all three reduced sulfur compounds in the concentration range of the applicable standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Base line separation is defined as a return to zero ±5 percent in the interval between peaks. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Administrator.

5.5.1 Calibration System. The calibration system must contain the following components.

5.5.2 Flow System. To measure air flow over permeation tubes at ±2 percent. Each flowmeter shall be calibrated after a complete test series with a wet test meter. If the flow measuring device differs from the wet test meter by 5 percent, the completed test shall be discarded. Alternatively, the tester may elect to use the flow data that would yield the lowest flow measurement. Calibration with a wet test meter before a test is optional.

5.5.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within ±1.1° C.

5.5.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within ±1° C.

6. Reagents

6.1 Fuel. Hydrogen (H_2) prepurified grade or better.

6.2 Combustion Gas. Oxygen (O_2) or air, research purity or better.

6.3 Carrier Gas. Prepurified grade or better.

6.4 Diluent. Air containing less than 0.5 ppm total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons.

6.5 Calibration Gases. Permeation tubes, one each of H_2S, COS, and CS_2, gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7. Pretest Procedures

The following procedures are optional but would be helpful in preventing any problem which might occur later and invalidate the entire test.

7.1 After the complete measurement system has been set up at the site and deemed to be operational, the following procedures should be completed before sampling is initiated.

7.1.1 Leak Test. Appropriate leak test procedures should be employed to verify the integrity of all components, sample lines, and connections. The following leak test procedure is suggested: For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull greater than 50 mm (2 in.) Hg vacuum, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for example) at each joint. Bubbling indicates the presence of a leak.

7.1.2 System Performance. Since the complete system is calibrated following each test, the precise calibration of each component is not critical. However, these components should be verified to be operating properly. This verification can be performed by observing the response of flowmeters or of the GC output to changes in flow rates or calibration gas concentrations and ascertaining the response to be within predicted limits. If any component or the complete system fails to respond in a normal and predictable manner, the source of the discrepancy should be identifed and corrected before proceeding.

8. Calibration

Prior to any sampling run, calibrate the system using the following procedures. (If more than one run is performed during any 24-hour period, a calibration need not be performed prior to the second and any subsequent runs. The calibration must, however, be verified as prescribed in section 10, after the last run made within the 24-hour period.)

8.1 General Considerations. This section outlines steps to be followed for use of the GC/FPD and the dilution system. The procedure does not include detailed instructions because the operation of these systems is complex, and it requires an understanding of the individual system being used. Each system should include a written operating manual describing in detail the operating procedures associated with each component in the measurement system. In addition, the operator shuld be familiar with the operating principles of the components; particularly the GC/FPD. The citations in the Bibliography at the end of this method are recommended for review for this purpose.

8.2 Calibration Procedure. Insert the permeation tubes into the tube chamber. Check the bath temperature to assure agreement with the calibration temperature of the tubes within ±0.1°C. Allow 24 hours for the tubes to equilibrate. Alternatively equilibration may be verified by injecting samples of calibration gas at 1-hour intervals. The permeation tubes can be assumed to have reached equilibrium when consecutive hourly samples agree within the precision limits of section 4.1.

Vary the amount of air flowing over the tubes to produce the desired concentrations for calibrating the analytical and dilution systems. The air flow across the tubes must at all times exceed the flow requirement of the analytical systems. The concentration in parts per million generated by a bube containing a specific permeant can be calculated as follows:

$$C = K \times P_r / ML$$

Equation 15-1

where:

C = Concentration of permeant produced in ppm.

P_r = Permeation rate of the tube in μg/min.

M = Molecular weight of the permeant: g/g-mole.

L = Flow rate, l/min, of air over permeant @ 20°C, 760 mm Hg.

K = Gas constant at 20°C and 760 mm Hg = 24.04 l/g mole.

8.3 Calibration of analysis system. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.05 to 1.0 ppm) for each of the four major sulfur compounds. Bypassing the dilution system, inject these standards in to the GC/FPD analyzers and monitor the responses. Three injects for each concentration must yield the precision described in section 4.1. Failure to attain this precision is an indication of a problem in the calibration or analytical system. Any such problem must be identified and corrected before proceeding.

8.4 Calibration Curves. Plot the GC/FPD response in current (amperes) versus their causative concentrations in ppm on log-log coordinate graph paper for each sulfur compound. Alternatively, a least squares equation may be generated from the calibration data.

8.5 Calibration of Dilution System. Generate a know concentration of hydrogen sulfied using the permeation tube system. Adjust the flow rate of diluent air for the first dilution stage so that the desired level of dilution is approximated. Inject the diluted calibration gas into the GC/FPD system and monitor its response. Three injections for each dilution must yield the precision described in section 4.1. Failure to attain this precision in this step is an indication of a problem in the dilution system. Any such problem must be identified and corrected before proceeding. Using the calibration data for H_2S (developed under 8.3) determine the diluted calibration gas concentration in ppm. Then calculate the dilution factor as the ratio of the calibration gas concentration before dilution to the diluted calibration gas concentration determined under this paragraph. Repeat this procedure for each stage of dilution required. Alternatively, the GC/FPD system may be calibrated by generating a series of three or more concentrations of each sulfur compound and diluting these samples before injecting them into the GC/FPD system. This data will then serve as the calibration data for the unknown samples and a separate determination of the dilution factor will not be necessary. However, the precision requirements of section 4.1 are still applicable.

9. Sampling and Analysis Procedure

9.1 Sampling. Insert the sampling probe into the test port making certain that no dilution air enters the stack through the port. Begin sampling and dilute the sample approximately 9:1 using the dilution system. Note that the precise dilution factor is that which is determined in paragraph 8.5. Condition the entire system with sample for a minimum of 15 minutes prior to commencing analysis.

9.2 Analysis. Aliquots of diluted sample are injected into the GC/FPD analyzer for analysis.

9.2.1 Sample Run. A sample run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

9.2.2 Observation for Clogging of Probe. If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if

the sample probe is clogged with particulate matter. If the probe is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning the probe or replacing it with a clean one. After each run, the sample probe must be inspected and, if necessary, dismantled and cleaned.

10. Post-Test Procedures

10.1 Sample Line Loss. A known concentration of hydrogen sulfide at the level of the applicable standard, ±20 percent, must be introduced into the sampling system at the opening of the probe in sufficient quantities to ensure that there is an excess of sample which must be vented to the atmosphere. The sample must be transported through the entire sampling system to the measurement system in the normal manner. The resulting measured concentration should be compared to the known value to determine the sampling system loss. A sampling system loss of more than 20 percent is unacceptable. Sampling losses of 0–20 percent must be corrected by dividing the resulting sample concentration by the fraction of recovery. The known gas sample may be generated using permeation tubes. Alternatively, cylinders of hydrogen sulfide mixed in air may be used provided they are traceable to permeation tubes. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

10.2 Recalibration. After each run, or after a series of runs made within a 24-hour period, perform a partial recalibration using the procedures in section 8. Only H_2S (or other permeant) need be used to recalibrate the GC/FPD analysis system (8.3) and the dilution system (8.5).

10.3 Determination of Calibration Drift. Compare the calibration curves obtained prior to the runs, to the calibration curves obtained under paragraph 10.1. The calibration drift should not exceed the limits set forth in paragraph 4.2. If the drift exceeds this limit, the intervening run or runs should be considered not valid. The tester, however, may instead have the option of choosing the calibration data set which would give the highest sample values.

11. Calculations

11.1 Determine the concentrations of each reduced sulfur compound detected directly from the calibration curves. Alternatively, the concentrations may be calculated using the equation for the least squares line.

11.2 Calculation of SO_2 Equivalent. SO_2 equivalent will be determined for each analysis made by summing the concentrations of each reduced sulfur compound resolved during the given analysis.

$$SO_2 \text{ equivalent} = \Sigma(H_2S, COS, 2\ CS_2)d$$

Equation 15-2

where:

SO_2 equivalent = The sum of the concentration of each of the measured compounds (COS, H_2S, CS_2) expressed as sulfur dioxide in ppm.

H_2S = Hydrogen sulfide, ppm.

COS = Carbonyl sulfide, ppm.

CS_2 = Carbon disulfide, ppm.

d = Dilution factor, dimensionless.

11.3 Average SO_2 equivalent will be determined as follows:

$$\text{Average } SO_2 \text{ equivalent} = \frac{\sum_{i=1}^{N} SO_2 \text{ equiv.}_i}{N\,(1 - Bwo)}$$

Equation 15-3

where:

Average SO_2 equivalent$_i$ = Average SO_2 equivalent in ppm, dry basis.

Average SO_2 equivalent$_i$ = SO_2 in ppm as determined by Equation 15-2.

N = Number of analyses performed.

Bwo = Fraction of volume of water vapor in the gas stream as determined by Method 4—Determination of Moisture in Stack Gases (36 FR 24887).

12. Example System

Described below is a system utilized by EPA in gathering NSPS data. This system does not now reflect all the latest developments in equipment and column technology, but it does represent one system that has been demonstrated to work.

12.1 Apparatus.

12.1.1 Sample System.

12.1.1.1 Probe. Stainless steel tubing, 6.35 mm (¼ in.) outside diameter, packed with glass wool.

12.1.1.2 Sample Line. 3/16 inch inside diameter Teflon tubing heated to 120° C. This temperature is controlled by a thermostatic heater.

12.1.1.3 Sample Pump. Leakless Teflon coated diaphragm type or equivalent. The pump head is heated to 120° C by enclosing it in the sample dilution box (12.2.4 below).

12.1.2 Dilution System. A schematic diagram of the dynamic dilution system is given in Figure 15-2. The dilution system is constructed such that all sample contacts are made of inert materials. The dilution system which is heated to 120° C must be capable of a minimum of 9:1 dilution of sample. Equipment used in the dilution system is listed below:

12.1.2.1 Dilution Pump. Model A-150 Kohmyhr Teflon positive displacement type, nonadjustable 150 cc/min. ±2.0 percent, or equivalent, per dilution stage. A 9:1 dilution of sample is accomplished by combining 150 cc of sample with 1350 cc of clean dry air as shown in Figure 15-2.

12.1.2.2 Valves. Three-way Teflon solenoid or manual type.

12.1.2.3 Tubing. Teflon tubing and fittings are used throughout from the sample probe to the GC/FPD to present an inert surface for sample gas.

12.1.2.4 Box. Insulated box, heated and maintained at 120° C, of sufficient dimensions to house dilution apparatus.

12.1.2.5 Flowmeters. Rotameters or equivalent to measure flow from 0 to 1500 ml/min. ±1 percent per dilution stage.

12.1.3.0 Gas Chromatograph.

12.1.3.1 Column—1.83 m (6 ft.) length of Teflon tubing, 2.16 mm (0.085 in.) inside diameter, packed with deactivated silica gel, or equivalent.

12.1.3.2 Sample Valve. Teflon six port gas sampling valve, equipped with a 1 ml sample loop, actuated by compressed air (Figure 15-1).

12.1.3.3 Oven. For containing sample valve, stripper column and separation column. The oven should be capable of maintaining an elevated temperature ranging from ambient to 100° C, constant within ±1° C.

12.1.3.4 Temperature Monitor. Thermocouple pyrometer to measure column oven, detector, and exhaust temperature ±1° C.

12.1.3.5 Flow System. Gas metering system to measure sample flow, hydrogen flow, oxygen flow and nitrogen carrier gas flow.

12.1.3.6 Detector. Flame photometric detector.

12.1.3.7 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

12.1.3.8 Power Supply. Capable of delivering up to 750 volts.

12.1.3.9 Recorder. Compatible with the output voltage range of the electrometer.

12.1.4 Calibration. Permeation tube system (Figure 15-3).

12.1.4.1 Tube Chamber. Glass chamber of sufficient dimensions to house permeation tubes.

12.1.4.2 Mass Flowmeters. Two mass flowmeters in the range 0-3 l/min. and 0-10 l/min. to measure air flow over permeation tubes at ±2 percent. These flowmeters shall be cross-calibrated at the beginning of each test. Using a convenient flow rate in the measuring range of both flowmeters, set and monitor the flow rate of gas over the permeation tubes. Injection of calibration gas generated at this flow rate as measured by one flowmeter followed by injection of calibration gas at the same flow rate as measured by the other flowmeter should agree within the specified precision limits. If they do not, then there is a problem with the mass flow measurement. Each mass flowmeter shall be calibrated prior to the first test with a wet test meter and thereafter at least once each year.

12.1.4.3 Constant Temperature Bath. Capable of maintaining permeation tubes at certification temperature of 30° C within ±0.1° C.

12.2 Reagents.

12.2.1 Fuel. Hydrogen (H_2) prepurified grade or better.

12.2.2 Combustion Gas. Oxygen (O_2) research purity or better.

12.2.3 Carrier Gas. Nitrogen (N_2) prepurified grade or better.

12.2.4 Diluent. Air containing less than 0.5 ppm total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons, and filtered using MSA filters 46727 and 79030, or equivalent. Removal of sulfur compounds can be verified by injecting dilution air only, described in section 8.3.

12.2.5 Compressed Air. 60 psig for GC valve actuation.

12.2.6 Calibration Gases. Permeation tubes gravimetrically calibrated and certified at 30.0° C.

12.3 Operating Parameters. The operating parameters for the GC/FPD system are as follows: nitrogen carrier gas flow rate of 100 cc/min, exhaust temperature of 110° C, detector temperature 105° C, oven temperature of 40° C, hydrogen flow rate of 80 cc/minute, oxygen flow rate of 20 cc/minute, and sample flow rate of 80 cc/minute.

12.4 Analysis. The sample valve is actuated for 1 minute in which time an aliquot of diluted sample is injected onto the separation column. The valve is then deactivated for the remainder of analysis cycle in which time the sample loop is refilled and the separation column continues to be foreflushed. The elution time for each compound will be determined during calibration.

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